[Second Edition.]

PATENT SPECIFICATION

Application Date : Oct. 26, 1931. *No. 29,689/31.* **391,444**

Complete Specification Left : Aug. 18, 1932.

Complete Specification Accepted : April 26, 1933.

PROVISIONAL SPECIFICATION.

Improvements in or relating to the Manufacture of Acetaldehyde.

We, BRITISH CELANESE LIMITED, a Company incorporated in accordance with the laws of Great Britain, of Celanese House, 22 & 23, Hanover Square, London, W.1, and WALTER HENRY GROOMBRIDGE, a subject of the King of Great Britain, of the Works of British Celanese Limited, Spondon, near Derby, do hereby declare the nature of this invention to be as follows:—

This invention relates to the manufacture of acetaldehyde from ethyl alcohol.

It is known that difficulties arise in oxidising ethyl alcohol to acetaldehyde in the gaseous phase, in particular it is difficult to master the reaction. Thus, it is very difficult to achieve uniform reaction or to prevent the development of excessive temperatures which lead to decomposition or to undesired products of excessive oxidation.

It has now been found that the oxidation of alcohol to aldehyde in the gaseous phase may be effected in an especially satisfactory manner, and particularly that uniform reaction may be attained and that the development of excessive temperatures with their resultant disadvantages may be largely or entirely avoided by introducing the air and alcohol, either together or separately, into the reaction zone in fractions or stages.

It has been found particularly advantageous to add the oxygen, air or other oxidising gas in fractions or stages to the alcohol vapour during the passage thereof through the converter or converters, catalyst bed or beds, as by such means not only may very uniform reaction be attained, but development of excessive temperatures with their resultant disadvantages can readily be avoided. The invention will be hereinafter described more particularly with reference to such a form of execution of the invention.

Initially the alcohol vapour may, if desired, contain small quantities of the oxidising gas (e.g. 5 to 20% or more of the total oxidising gas to be employed), the remainder of the oxidising gas being added in stages or fractions as before indicated. The total quantity of oxidising gas used may be smaller than or equal to or even greater than that theoretically requisite to oxidise the whole of the alcohol vapour to aldehyde.

The addition of the fractions of the oxidising gases to the alcohol vapour in the passage thereof through the converters, catalyst belts or the like may be effected in any convenient way. If desired the fractions may be introduced at temperatures below those obtaining in the stream of reaction vapours at the particular points of introduction of the fractions, in which case the cooling effect of the cold or relatively cold incoming fractions may be utilised to assist the maintenance of uniform temperature, or a range of temperature, throughout the converter or catalyst.

The alcohol vapours and/or the oxidising gases may, if desired, be diluted with any indifferent diluent gases, such for instance as nitrogen, carbon dioxide, steam, the use of steam being especially advantageous.

Whilst the invention has been described more particularly with reference to a form wherein the oxygen, air or other oxidising gas is added in fractions or stages to the alcohol vapour during the passage thereof through the converter or catalyst, the invention is not limited to such a form of execution, but contemplates all forms of execution wherein the alcohol vapour and oxidising gas are introduced severally or together in fractions or stages into the reaction zone. For instance, mixtures of oxidising gas and alcohol may be introduced in stages or fractions at different points in the reaction zones or levels in the catalyst belts or beds. Or, for instance, the alcohol vapour may be introduced in fractions or stages into a stream of oxidising gas (preferably diluted with steam and/or indifferent gases) passing through the converter or catalyst; in such case, however, the control of the reaction temperature is usually more difficult.

In any forms of execution of the invention indifferent diluents such as nitrogen, steam or the like may, if desired, be admixed with the reaction gases or vapours, whether by admixture with the fractions to be introduced or otherwise.

[*Price* 1/-]

Price 4s 6d.

The process of the invention may be performed in the presence of any catalysts capable of promoting the oxidation of alcohol to aldehyde, silver, copper, silver oxide or copper oxide being especially useful catalysts. The reaction may be performed at any temperatures suitable for the oxidation of alcohol to aldehyde. In general, however, temperatures between about 250° and 500° C. are very useful for the purpose of the invention, temperatures between about 350°—400° and 450° C. being especially useful.

Dated this 26th day of October, 1931.

STEPHENS & ALLEN,
Chartered Patent Agents,
Celanese House, 22 & 23, Hanover Square,
London, W.1.

COMPLETE SPECIFICATION

Improvements in or relating to the Manufacture of Acetaldehyde.

We, BRITISH CELANESE LIMITED, a Company incorporated in accordance with the laws of Great Britain, of Celanese House, 22 & 23, Hanover Square, London, W.1, and WALTER HENRY GROOMBRIDGE, a subject of the King of Great Britain, of the Works of British Celanese Limited, Spondon, near Derby, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the manufacture of acetaldehyde from ethyl alcohol.

Oxidation of ethyl alcohol can produce acetaldehyde, acetic acid and oxides of carbon according to the degree of oxidation to which the alcohol is subjected. The manufacture of acetaldehyde by oxidising ethyl alcohol is therefore a matter of great difficulty because of the production of acetic acid and oxides of carbon which takes place even when the quantities of alcohol and oxygen which are theoretically required for the production of acetaldehyde are employed. The development of excessive temperatures either locally or throughout the reaction zone not only aggravates these difficulties but also leads to the production of undesired decomposition products.

According to the process of the present invention the manufacture of acetaldehyde by oxidising ethyl alcohol in the vapour phase is carried out by a process in which all or part of the oxygen and/or the ethyl alcohol is introduced into the reaction zone at a number of points spaced along the reaction zone or in parallel to the line of flow of the reactants through the reaction zone.

It has previously been proposed to carry out exothermic gas reactions, especially the synthesis of ammonia from its elements and processes of oxidation such as the combustion of ammonia to nitric acid, effected by the contact of gases with solid catalytic material by a method comprising dividing the gas supply pipe into several branches and uniformly distributing the discharge openings of the said branches over the length of the catalytic tube. The present invention is concerned solely with the manufacture of acetaldehyde by the oxidation of ethyl alcohol in the vapour phase.

The invention is more particularly concerned with processes in which the reaction zone is a catalyst belt, bed or layer and a particularly important embodiment of the invention consists in supplying all or part of the oxygen and/or alcohol to the catalyst by means of perforated pipes or other members arranged or adapted to introduce the same into the catalyst through perforations in the pipes or members arranged in or parallel to the line of flow of the reactants through the catalyst.

The perforated members may be disposed in or around the catalyst and they may be disposed both in and around the catalyst. In order that the oxygen and/or alcohol should be introduced in as uniform a manner as possible it is advantageous, particularly when thick or long catalyst belts, beds or layers are employed, to arrange that the members introduce the oxygen or alcohol to a large number of points of the catalyst and to introduce the oxygen or alcohol over a substantial part of the catalyst along the line of flow.

The perforated members may, for example, be constituted by a number of perforated pipes disposed within or extending through the catalyst belt, bed or layer or a plurality of such catalyst belts, beds or layers, or for instance, whether or not such pipes are provided, the catalyst may be surrounded by a perforated shell or the like through which the gases or vapours to be introduced may pass laterally into the catalyst.

As above stated all or part of the oxygen and/or alcohol to be subjected to the reaction may be introduced through the perforated pipes or members. It is, however, preferred to introduce the oxygen

(whether pure or in the form of a gas mixture e.g. air) or a part of the oxygen by the perforated pipes or members, the alcohol vapour to be oxidised being passed through the catalyst belt, bed or layer or plurality thereof. The alcohol may if desired contain small quantities of oxygen (e.g. 10—20%) or more of the total to be employed; the remainder being added in stages or fractions as before indicated. The total quantity of oxygen used may be smaller than or equal to or even greater than that theoretically requisite for the oxidation of the whole of the alcohol vapour to acetaldehyde.

The reactants or either of the reactants may, if desired, be diluted with any indifferent gases such, for instance, as nitrogen, carbon dioxide or steam, dilution with steam being especially advantageous.

Any catalysts capable of promoting the oxidation may be employed, silver, copper, silver oxide and copper oxide being especially useful catalysts. The reaction may be performed at any temperatures suitable for the oxidation of alcohol to aldehyde. In general, temperatures between about 250° and 500° C. are very useful for the purposes of the invention, temperatures between about 350°—400° and 450° C. being especially useful.

Any convenient means for cooling or heating the catalyst or for controlling the reaction temperature may be provided. For instance, there may be used with advantage as cooling or temperature controlling means hollow heat exchanging elements arranged within the catalyst or reaction zone and supplied with water or other cooling fluids. Particularly effective control of the reaction can be attained by the methods described in Specifications Nos. 26,630/31 (Serial No. 390,186) and 26,631/31 (Serial No. 390,504) of British Celanese Limited, H. F. Oxley and W. H. Groombridge. According to Specification No. 26,630/31 (Serial No. 390,186) exothermic chemical reactions are controlled by placing in heat exchange with the reaction zone a climbing film of cooling liquid which liquid is supplied at such a rate that aids evaporation or aids the formation of the climbing film. According to Specification No. 26,631/31 (Serial No. 390,504) the control of exothermic chemical reactions is effected by removing the heat from the reaction zone by vaporisation of a liquid in heat exchange with the reaction zone and by removing the vapour generated from said liquid by a path passing downwardly through the body of said liquid.

If desired the reactant or reactants may be introduced at temperatures below those obtaining in the stream of the reaction vapours at the particular points of introduction of the fractions in which case the cooling effect of the cold or relatively cold incoming fractions may be utilised to assist the maintenance of uniform temperature or a range of temperature throughout the converter or catalyst.

By means of the invention very uniform reaction can readily be achieved. Moreover the invention greatly facilitates control of the reaction. The invention enables local or other overheating of the reaction gases and consequent lowering of yield to be readily avoided, and the risk of formation of decomposition products or products of too-far reaching reaction can be greatly reduced or eliminated.

The accompanying drawings show diagrammatically apparatus suitable for use in carrying out the process of the present invention.

Figure 1 shows an apparatus suitable for use when the reactants are supplied to the catalyst separately.

Figure 2 shows an apparatus suitable for use when the reactants are supplied to the catalyst in admixture.

In Figure 1 the reaction vessel 1 contains a catalyst bed 2 traversed by cooling members 3 consisting of pairs of concentric tubes, the outer tubes 4 being closed at the top end and connected to a water box 6 having a water inlet 7 and the inner tubes 5 extending to and opening into the closed end of the outer tubes 4 and connected to a steam box 8 having a steam outlet 9. The catalyst bed 2 is also traversed by tubes 10 interspaced with the cooling members 3 and provided with perforations 18; the perforated tubes 10 are closed at the lower end and are carried at the upper end by a tube plate 11 above which there is a chamber 12 having a reactant supply-pipe 13. The space 14 between the top of the catalyst bed 2 and the tube plate 11 is in connection with a second reactant inlet 15 whilst the space 16 between the base of the catalyst bed 2 and the top of the water box 6 is in connection with an outlet 17. A perforated plate 19 is provided to distribute uniformly over the catalyst bed 2 the reactant supplied at 15, the attainment of this object being facilitated by the employment of more than one inlet 15 disposed around reaction vessel 1.

In operation ethyl alcohol vapour, supplied to the reaction vessel 1 by means of the inlet 15, passes by way of the perforated plate 19 to and through the catalyst bed 2 where it meets oxygen or air entering the catalyst bed from the perforations 18 in the tube 10, the air being supplied to the tubes 10 from the chamber 12 fed

by the inlet 13. Oxidation of the alcohol vapour ensues in the catalyst zone the temperature of which is maintained within the desired limits, preferably about 350—400° C., by means of the cooling members 3 by a climbing film of water in the annular space between the outer tubes 4 and the inner tubes 5 as described in Specification No. 26,630/31 (Serial No. 390,186). Initially a heating medium, e.g. steam may be passed through the member 3 to start the reaction. Acetaldehyde together with any unchanged alcohol and gases leave the reaction zone by the outlet 17 and are treated to separate the acetaldehyde.

Figure 2 shows the apparatus shown in Figure 1 modified so as to be suitable for employment when a mixture of the reactants is to be supplied to the catalyst. The perforated tubes 10 end at the perforated plate 19 opening into the chamber 12 having an inlet 13.

In operation a mixture or alcohol vapour and oxygen and any diluents which it is desired to employ is supplied by the inlet 13 to the chamber 12 from which part of the mixture passes by the perforations in the plate 19 to the catalyst 2 whilst the remainder passes through the tubes 10 and is distributed in fractions throughout the catalyst 2 by means of the perforations 18.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. The manufacture of acetaldehyde by oxidation of ethyl alcohol in the vapour phase wherein all or part of the oxygen and/or ethyl alcohol vapour is introduced into the reaction zone at a number of points spaced along the reaction zone in or parallel to the line of flow of the reactants through the reaction zone.

2. Process according to claim 1, wherein all or part of the oxygen and/or ethyl alcohol is introduced by means of conduits arranged or adapted to deliver oxygen and/or alcohol to the reaction zone at a number of points spaced along the reaction zone in or parallel to the line of flow of the reactants through the reaction zone.

3. Process according to claim 2, wherein the conduits are perforated pipes traversing the reaction zone.

4. Process according to any of the preceding claims wherein the oxygen or other oxidising gas is supplied in fractions or stages.

5. Process according to any of the preceding claims wherein the reaction zone contains a catalyst.

6. The manufacture of acetaldehyde substantially as hereinbefore described.

7. Acetaldehyde whenever produced by any of the processes claimed in the preceding claims.

8. In the manufacture of acetaldehyde according to any of the processes claimed in the preceding claims the use of apparatus substantially as described with reference to the accompanying drawings.

Dated this 12th day of August, 1932.

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Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 8138.—50/8/1939.]

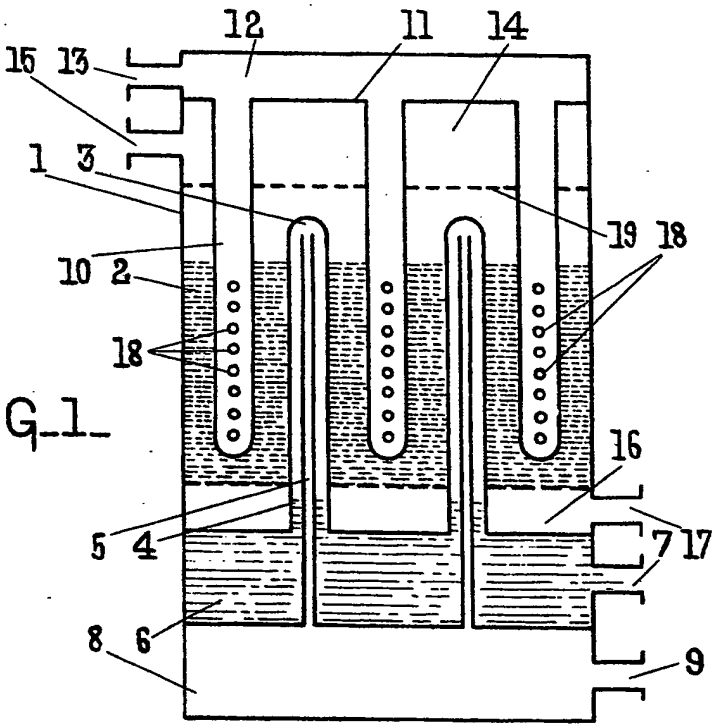

FIG. 1.

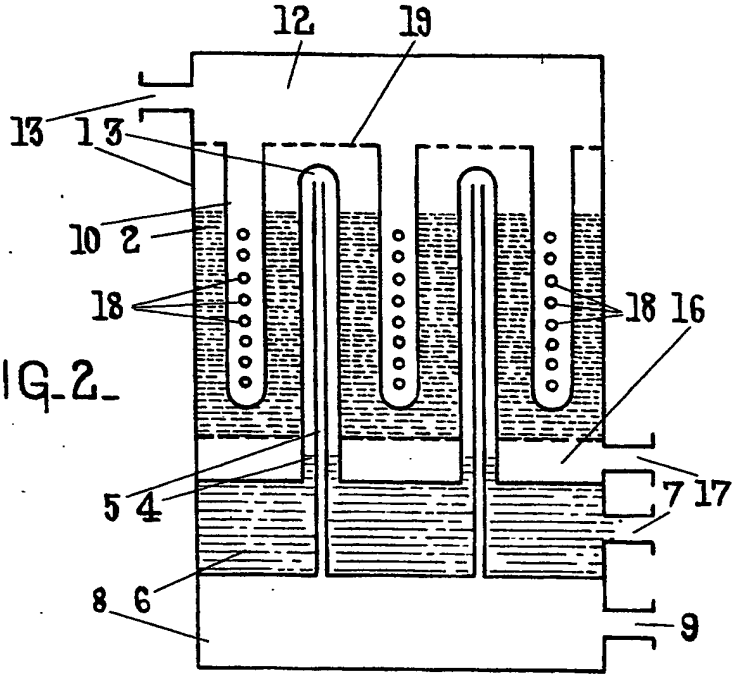

FIG. 2.

Malby & Sons Photo-Litho.